

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-081355

(43)Date of publication of application : 27.03.2001

(51)Int.Cl.

C09C 1/56
C09D 11/02

(21)Application number : 11-263497

(71)Applicant : TOKAI CARBON CO LTD

(22)Date of filing : 17.09.1999

(72)Inventor : ARAI HIROAKI
KONO MASATAKA

(54) CARBON BLACK PIGMENT FOR AQUEOUS INK

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a carbon black pigment highly dispersible in water and suitable for aqueous black inks.

SOLUTION: This carbon black pigment for aqueous inks has the following characteristics: nitrogen adsorption specific surface area (N2SA) is 160-200 m²/g; iodine adsorption(IA) is 140-190 mg/g; N2SA/IA is 0.96-1.20; CTAB specific surface area is 140-170 m²/g; DBP oil absorption is 100-140 mL/100 g; 24M4DBP oil absorption is 90-110 mL/100 g; tinting strength (Tint) is ≥ 120 ; the ratio of total oxygen atom to total carbon atom (oxygen bond energy intensity/carbon bond energy intensity) determined by X-ray photoelectron spectroscopy is ≥ 0.1 ; the mode diameter D_{st} of the aggregate's Stokes-equivalent diameter distribution is 50-70 nm; half-value width ΔD_{st} is ≤ 60 nm; agglomerate's mean diameter D_{upa50%} is 60-110 nm; and agglomerate's maximum diameter D_{upa99%} is ≤ 250 nm.

LEGAL STATUS

[Date of request for examination] 26.12.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

EXPRESS MAIL LABEL

NO.: EV 481671937 US

* NOTICES *

JPO and NCIPJ are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] 160–200m²/g and the iodine amount of adsorption (IA) 140 – 190 mg/g, [nitrogen adsorption specific surface area (N₂SA)] 0.96–1.20, and CTAB specific surface area 140–170m²/g, [the value of N₂ SA/IA] 100–140ml / 100g, and 24M4DBP oil absorption 90–110ml / 100g, [DBP oil absorption] Tinting strength (Tint) is carbon black of or more 120**. The carbon black pigment for water color ink characterized by the atomic ratio (reinforcement of the reinforcement / carbon to carbon bond energy of oxygen binding energy) of the total carbon atom and all the oxygen atoms which were measured by X-ray photoelectron spectroscopy being 0.1 or more.

[Claim 2] The carbon black pigment for water color ink according to claim 1 with which the value whose value of 60nm or less and mean-particle-diameter Dupa50% of agglomerate half-value-width deltaDst [in / in the mode diameter Dst of stokes nominal diameter distribution of an aggregate / 50–70nm and an isomerism cloth] is 60–110nm and maximum grain size Dupa99% of agglomerate has the shape of corpuscular character 250nm or less. However, Dst is a centrifuge (DCF). The stokes nominal diameter of the maximum frequency in stokes nominal diameter distribution of the aggregate measured and deltaDst irradiate laser light at the water dispersion of carbon black to half-value width and Dupa50% of this stokes nominal diameter distribution, and Dupa99% shows the value [in / for the value of 50% cumulative frequency in the cumulative frequency distribution curve of the agglomerate particle size created from the frequency modulation degree of the scattered light / an isomerism cloth curve] of 99% cumulative frequency.

[Translation done.]

* NOTICES *

JPO and NCIPJ are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.***** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is excellent in underwater dispersibility ability, and relates to the carbon black pigment for water color ink suitable as an object for aqueous black ink.

[0002]

[Description of the Prior Art] Since wettability [as opposed to water at hydrophobicity] of carbon black is low, it is very difficult to distribute stability by high concentration to underwater. This originates in that there are very few functional groups with high compatibility with the water molecule which exists in a carbon black front face. Then, the approach of carrying out oxidation reforming of the carbon black, and forming the functional group of a hydrophilic property in a front face is learned for many years.

[0003] For example, to JP,48-18186,A, carbon black is oxidized in the water solution of the following ** halogen acid salt, and in more nearly subsequently than the system of reaction carrying out separation uptake of the oxidization carbon black, the manufacture approach of water-dispersion reforming carbon black that the manufacture approach of the oxidization carbon black characterized by washing by the organic solvent is characterized by carrying out low-temperature-oxidation plasma treatment of the carbon black to JP,57-159856,A again is indicated.

[0004] Useful [of the carbon black excellent in water-dispersion] is carried out as watercolor pigment ink, it begins a writing implement, and attracts attention also as recording ink especially for ink jet printers etc. in recent years. In the watercolor pigment ink which contains water and carbon black in JP,8-3498,A as water color ink using easy water dispersible carbon black, It sets to the manufacture approach of the watercolor pigment ink in which this carbon black has the surface activity hydrogen content of 1.5 or more mmol/g, and the watercolor pigment ink containing water and carbon black, and is (a). The process which obtains acid carbon black, and (b) The manufacture approach of the watercolor pigment ink which includes the process which oxidizes said acid carbon black further with the following ** halogen acid salt underwater is proposed. Moreover, in JP,8-319444,A, they are the oil absorption of 100ml / 100g. The manufacture approach of the watercolor pigment ink which includes process; which oxidizes this carbon black using process; and the following ** halogen acid salt which carry out differential powder of the following carbon black into an aqueous medium is indicated.

[0005] In above-mentioned JP,8-3498,A and above-mentioned JP,8-319444,A, carbon black is oxidized, and by making a front face contain many active hydrogen which is the functional group of a hydrophilic property, water-dispersion is good and obtains watercolor pigment ink excellent in prolonged distributed stability. However, in order for carbon black to distribute underwater and to maintain a stable distributed condition, it is difficult to judge the quality of dispersibility exactly only by regulating the amount of functional groups to which the amount of functional groups of the hydrophilic property which exists in the contact interface of a carbon black particle front face and a water molecule functions greatly, and only exists in per carbon black unit weight.

[0006] Then, this invention persons advanced research paying attention to the amount of

hydrogen content functional groups of the hydrophilic property which considers as the new index which judges the quality of dispersibility ability exactly, and exists in per carbon black unit surface area, and developed and proposed the easy water dispersible carbon black whose amounts of total of a carboxyl group and hydroxyl are two or more 3microeq/m per unit surface area, and its manufacture approach among the hydrogen content functional groups which exist in a front face (JP,11-148027,A).

[0007]

[Problem(s) to be Solved by the Invention] this invention persons advanced research about easy water dispersible carbon black succeedingly, and succeeded in development of a carbon black pigment suitable as ink for printers, such as water color ink, for example, bubble jet etc., using these easy water dispersible carbon black as a black pigment.

[0008] That is, the purpose of this invention is to offer the carbon black pigment excellent in paper fixing concentration, printing grace, regurgitation stability, lightfastness, preservation stability, etc. for water color ink, when printing to a form, an OHP sheet, art paper, etc. chiefly, a regular paper and.

[0009]

[Means for Solving the Problem] The carbon black pigment for water color ink of this invention for attaining the above-mentioned purpose 160-200m²/g and the iodine amount of adsorption (IA) 140 - 190 mg/g, [nitrogen adsorption specific surface area (N₂SA)] 0.96-1.20, and CTAB specific surface area 140-170m²/g, [the value of N₂ SA/IA] 100-140ml / 100g, and 24M4DBP oil absorption 90-110ml / 100g, [DBP oil absorption] Tinting strength (Tint) is carbon black of or more 120**, and it is characterized by the atomic ratio (reinforcement of the reinforcement / carbon to carbon bond energy of oxygen binding energy) of the total carbon atom and all the oxygen atoms which were measured by X-ray photoelectron spectroscopy being 0.1 or more on a configuration.

[0010] Moreover, the carbon black pigment for water color ink of this invention is carbon black equipped with the above-mentioned property, and the mode diameter D_{st} of stokes nominal diameter distribution of an aggregate is characterized by the value whose value of 60nm or less and mean-particle-diameter D_{upa50%} of agglomerate half-value-width ΔD_{st} in 50-70nm and an isomerism cloth is 60-110nm and maximum grain size D_{upa99%} of agglomerate having the shape of corpuscular character 250nm or less on a configuration. However, D_{st} is a centrifuge (DCF). The stokes nominal diameter of the maximum frequency in stokes nominal diameter distribution of the aggregate measured and ΔD_{st} irradiate laser light at the water dispersion of carbon black to half-value width and D_{upa50%} of this stokes nominal diameter distribution, and D_{upa99%} shows the value [in / for the value of 50% cumulative frequency in the cumulative frequency distribution curve of the agglomerate particle size created from the frequency modulation degree of the scattered light / an isomerism cloth curve] of 99% cumulative frequency.

[0011]

[Embodiment of the Invention] The property range of carbon black is regulated as mentioned above, because the paper fixing concentration at the time of printing when it considered as water color ink for N₂ SA to be under 160m²/g, and the rate of precipitate residue increased, filterability and regurgitation stability fell remarkably and 200m²/g was exceeded becomes low. Moreover, there is little volatile matter (surface functional group) of carbon black that the value of N₂ SA/IA is less than 0.96, wettability with an oxidizer water solution worsens and dispersibility falls. However, if the value of N₂ SA/IA exceeds 1.20, the unburnt matter of carbon black will cause many trouble to wettability with an oxidizer water solution, oxidation is not fully performed, but dispersibility falls.

[0012] If the area of liquid-***** becomes it small that CTAB specific surface area is under 140m²/g, and a problem is produced to filterability and the rate of precipitate residue and 170m²/g is exceeded, the area of liquid-***** will become large and dispersibility will become inadequate. DBP oil absorption is 100ml / 100g. Printing concentration becomes it thin that it is the following, and they are 140ml / 100g. If it exceeds, the rate of precipitate residue will increase and filterability will fall. 24M4DBP is 90ml / 100g. Printing concentration falls that it is

the following and they are 110ml / 100g. If it exceeds, the rate of precipitate residue will increase and filterability and preservation stability will become a defect. Tint Whenever [grain / which is less than 120], since broadcloth [distribution], filterability and the rate of precipitate residue become a defect.

[0013] In addition to these property range, the carbon black pigment of this invention is characterized by the point that the value of the atomic ratio (reinforcement of the reinforcement / carbon to carbon bond energy of oxygen binding energy) of the total carbon atom and all the oxygen atoms which were measured by X-ray photoelectron spectroscopy is 0.1 or more as an amount of functional groups which exists in the front face. When self-dispersibility [as opposed to / that the intensity ratio (atomic ratio) of the reinforcement / carbon to carbon bond energy of the oxygen binding energy measured by X-ray photoelectron spectroscopy, such as XPS and ESCA is less than 0.1 / polar solvents, such as water,] falls remarkably and considers as water color ink, preservation stability gets worse extremely. In addition, accommodation of this intensity ratio makes a carbon black particle front face oxidize chemically by oxidation treatment, and is performed by giving a hydrophilic functional group by carrying out chemical modification.

[0014] Oxidation treatment is performed by adding carbon black and oxidizing in oxidizing agent water solutions, such as alkali-metal salts, such as a hypochlorite, chlorite, a chlorate, persulfate, a perboric acid salt, and percarbonate, and ammonium salt, controls suitably the concentration of an oxidizing agent water solution, the addition of carbon black, reaction temperature, reaction time, etc., and it is processed so that the atomic ratio (reinforcement of the reinforcement / carbon to carbon bond energy of oxygen binding energy) of a total carbon atom and all oxygen atoms may become 0.1 or more.

[0015] Furthermore, the carbon black pigment for water color ink of this invention is carbon black equipped with the above-mentioned property, and it is more desirable that the value whose value of 60nm or less and mean-particle-diameter Dupa50% of agglomerate half-value-width ΔD_{50} [in / in the mode diameter Dst of stokes nominal diameter distribution of an aggregate / 50-70nm and an isomerism cloth] is 60-110nm and maximum grain size Dupa99% of agglomerate has the shape of corpuscular character 250nm or less.

[0016] The agglomerate particle size in a moisture powder condition becomes it small that the mode diameter Dst of stokes nominal diameter distribution of an aggregate is less than 50nm, whenever [black] falls, on the other hand, if 70nm is exceeded, although whenever [black] improves, the rate of precipitate residue will increase, and filterability will fall. Moreover, the diameter distribution of a grain whose half-value-width ΔD_{50} exceeds 60nm becomes broadcloth, whenever black, the rate of precipitate residue increases and filterability becomes a defect.

[0017] Moreover, as for making the value of 60-110nm and maximum grain size Dupa99% of agglomerate into the shape of corpuscular character 250nm or less, carbon black passes the value of mean-particle-diameter Dupa50% of agglomerate from the clearance between paper fiber as Dupa50% of value is less than 60nm, and paper fixing concentration falls. Although whenever [black] will improve on the other hand if 110nm is exceeded, it is for filterability and the rate of precipitate residue to get worse. Moreover, if Dupa99% of value exceeds 250nm, the rate of precipitate residue will increase and regurgitation stability and a filterable fall will become remarkable.

[0018] In addition, the value from which mean-particle-diameter Dupa50% of this agglomerate and maximum grain size Dupa99% were obtained by the following measuring method is used. Carbon black is distributed in water and it is 0.1 - 0.5 g/l. Dispersion liquid are prepared, laser light is irradiated at dispersion liquid using a heterodyne laser Doppler system particle-size-distribution measuring device (micro truck company make, UPAmode19340), and the particle size of the agglomerate in dispersion liquid is measured from the degree of the frequency modulation of the scattered light. Brownian motion of the carbon black in dispersion liquid is carried out, and the frequency of the scattered light becomes irregular with the magnitude of the carbon black floc currently distributed according to the Doppler effect. Therefore, since the violence of the Brownian motion by the magnitude of floc differs, the magnitude of the floc in the condition of

distributing underwater, i.e., the particle size of agglomerate, can be measured. Thus, the cumulative frequency distribution curve is created from the measured agglomerate particle size, and mean-particle-diameter Dupa50% of agglomerate (nm) and the value of 99% cumulative frequency are made into maximum grain size Dupa99% of agglomerate (nm) for the value of cumulative frequency 50%.

[0019] Water color ink is obtained by making it distribute by desired concentration in aqueous media, such as water, by using carbon black equipped with these properties as a black pigment. That is, pH of the water dispersion which distributed carbon black is adjusted to 6-11, and separation purification of the residual salt is carried out by electrodialysis or demarcation membranes (a reverse osmotic membrane, ultrafiltration membrane, loose R.O, etc.). In addition, the residual salt concentration in carbon black dispersion liquid makes carbon black content concentration 20%, and conductivity is 5 mS/cm. It is desirable to carry out separation purification so that it may become the following. Moreover, in order to plan distributed stability as water color ink, it is desirable to adjust a ** carbon black pigment to the concentration not more than 60wt%.

[0020] Hereafter, the example of this invention is concretely explained as contrasted with the example of a comparison.

[0021] Carbon black 100g of the property shown in one to examples 1-3 and example of comparison 4 table 1 It adds in 3000ml of persulfuric acid soda water solutions with a concentration of 2.2 Ns, and they are the reaction temperature of 60 degrees C, reaction-time 10 hours, and agitating speed 300rpm. It oxidized. Subsequently, the carbon black carried out the ** exception was distributed in pure water, the sodium-hydroxide water solution neutralized, after separating the salt which carries out purification processing by ultrafiltration membrane, and remains, it filtered and carbon black was separated, rinsing desiccation was carried out and the sample of a carbon black pigment was produced. They are oxygen binding energy reinforcement and carbon to carbon bond energy intensity about these carbon black samples Surface Science Instruments Shrine make It measured with S-Probe ESCA 2803 mold, and the atomic ratio of a total carbon atom and all oxygen atoms was written together to Table 1.

[0022] It oxidized by example of comparison 5 ozone, and also the carbon black sample was produced by the same approach as an example, the binding energy was measured, and the atomic ratio of a total carbon atom and all oxygen atoms was written together to Table 1.

[0023]

[Table 1]

| 例No. 特性 | 実 施 例 | | | 比 較 例 | | | | |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| IA | 144 | 180 | 173 | 120 | 123 | 160 | 130 | 144 |
| N ₂ SA | 170 | 178 | 181 | 135 | 119 | 160 | 134 | 170 |
| N ₂ SA/IA | 1.181 | 0.989 | 1.046 | 1.125 | 0.967 | 1.000 | 1.031 | 1.181 |
| CTAB | 160 | 152 | 159 | 128 | 111 | 150 | 130 | 160 |
| DBP | 115 | 131 | 130 | 56 | 123 | 65 | 104 | 115 |
| 24M4DBP | 100 | 98 | 101 | 49 | 92 | 58 | 90 | 100 |
| Tint | 141 | 137 | 131 | 145 | 126 | 140 | 129 | 141 |
| Dst (nm) | 61 | 58 | 69 | 47 | 68 | 50 | 62 | 61 |
| Δ Dst (nm) | 44 | 40 | 51 | 32 | 40 | 35 | 48 | 44 |
| Dupa50%(nm) | 90.5 | 96.3 | 106.3 | 41.5 | 132.1 | 32.1 | 124.5 | 265.4 |
| Dupa99%(nm) | 195.4 | 214.2 | 230.1 | 162.3 | 329.2 | 145.2 | 254.1 | 457.1 |
| 原子比 | 0.34 | 0.33 | 0.35 | 0.33 | 0.32 | 0.33 | 0.34 | 0.05 |

[0024] Next, these carbon black samples were distributed by 20% of the weight of concentration in pure water as a pigment, water color ink was prepared, and the following approach estimated dispersibility ability and the ink engine performance. The obtained result was shown in Table 2.

[0025] ** warming — stability; — a sample — a well-closed container — putting — the inside of a 70-degree C attemperator — the viscosity change for one to four weeks — measuring — warming — the distributed stability at the time was compared. In addition, viscosity was measured with the rotational-vibration type viscometer [Yamaichi Electronics make and VM-100 A-L].

[0026] ** particle diameter measurement; — a sample and warming — it measured using the heterodyne laser Doppler system particle-size-distribution measuring device [micro truck company make and UPA model9340] about the particle diameter of the sample which examined stability. If a laser beam is applied to the particle which is carrying out Brownian motion into suspension, the frequency of the scattered light will modulate this measuring device according to the Doppler effect. The violence of Brownian motion, i.e., particle diameter, is measured from the modulation degree of the frequency.

[0027] ** Printing concentration; the carbon black distribution concentration of water color ink is diluted to 4% of the weight, use XEROX 4024 paper as copy paper, print by #6 bar coder to this, and it is Macbeth concentration meter [COL mho gene company make. Optical density was measured using RD-927].

[0028] ** Filterability; watercolor pigment ink 200g The filter paper (NO.2) and film aperture of 90phi 3 micrometers 0.8 mum and 0.65 micrometers 0.45 micrometers The filtration trial was performed under reduced pressure of 20Torr(s) using the filter, and through put was measured.

[0029] ** rate of precipitate residue; — weight ratio (M1/M0) of the amount of precipitate residue (M1) after performing at-long-intervals alignment separation processing for aquosity black ink with the gravitational acceleration of 20000G for 30 minutes, and the weight (M0) of the carbon black before centrifugal separation processing It considered as the rate of precipitate residue. Distributed stability becomes good, so that this value is low.

[0030]

[Table 2]

| 例No. | | 実施例 | | | 比較例 | | | | |
|----------------------|---------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| 保存安定性 | 初期粘度(cp) | 3.34 | 3.65 | 3.12 | 2.54 | 3.14 | 3.34 | 3.65 | 8.51 |
| | 70℃、1 W後(cp) | 3.34 | 3.65 | 3.11 | 2.54 | 3.14 | 3.34 | 3.65 | ゲル化 |
| | 70℃、2 W後(cp) | 3.31 | 3.65 | 3.10 | 2.53 | 3.13 | 3.31 | 3.65 | — |
| | 70℃、3 W後(cp) | 3.30 | 3.59 | 3.08 | 2.53 | 3.13 | 3.30 | 3.59 | — |
| | 70℃、4 W後(cp) | 3.28 | 3.57 | 3.07 | 2.53 | 3.13 | 3.28 | 3.57 | — |
| 平均粒径 | 初期平均粒径(nm) | 90.5 | 96.3 | 106.3 | 41.5 | 132.1 | 32.1 | 124.5 | 265.4 |
| | 70℃、1 W後(nm) | 90.1 | 96.2 | 106.2 | 41.5 | 131.8 | 32.1 | 124.5 | ゲル化 |
| | 70℃、2 W後(nm) | 89.9 | 96.1 | 106.2 | 41.4 | 131.7 | 32.1 | 124.4 | — |
| | 70℃、3 W後(nm) | 89.7 | 96.1 | 106.2 | 41.3 | 131.7 | 32.0 | 124.3 | — |
| | 70℃、4 W後(nm) | 89.5 | 96.1 | 106.1 | 41.2 | 131.5 | 32.0 | 124.3 | — |
| 最大粒径 | 初期最大粒径(nm) | 195.4 | 214.2 | 230.1 | 162.3 | 329.2 | 145.2 | 254.1 | 457.1 |
| | 70℃、1 W後(nm) | 195.3 | 214.2 | 230.0 | 162.1 | 329.1 | 145.2 | 254.1 | ゲル化 |
| | 70℃、2 W後(nm) | 195.3 | 214.1 | 229.9 | 161.9 | 328.8 | 145.2 | 254.1 | — |
| | 70℃、3 W後(nm) | 195.2 | 214.1 | 229.8 | 161.8 | 328.8 | 145.1 | 254.0 | — |
| | 70℃、4 W後(nm) | 195.2 | 214.0 | 229.8 | 161.7 | 328.8 | 145.1 | 254.0 | — |
| 濾過性 % | No.2濾紙 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 0 |
| | 膜孔径 (3 μm) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 0 |
| | 膜孔径 (0.8 μm) | 100 | 100 | 100 | 100 | 80 | 100 | 100 | 0 |
| | 膜孔径 (0.65 μm) | 100 | 100 | 100 | 100 | 0 | 100 | 5 | 0 |
| | 膜孔径 (0.45 μm) | 50 | 80 | 45 | 50 | 0 | 70 | 0 | 0 |
| 印字濃度 ; コピー紙 (OD値) | | 1.41 | 1.45 | 1.46 | 0.98 | 1.47 | 0.92 | 1.44 | 1.58 |
| 沈殿残滓率 (%) | | 11.3 | 14.5 | 17.9 | 12.5 | 27.1 | 11.1 | 24.1 | 67.2 |

[0031] although the water color ink which was distributed and prepared the carbon black pigment of an example from the result of Tables 1 and 2 has the outstanding preservation stability, filterability, paper fixing concentration, and a rate of precipitate residue — the example 1 of a comparison — IA, N2 SA, CTAB, DBP, and 24M4 — although filterability, preservation stability, and the rate of precipitate residue are good since DBP and Dst are also small, paper fixing concentration is remarkably low. Although preservation stability and paper fixing concentration are good since the example 2 of a comparison has IA, N2 SA, and CTAB out of range, filterability and the rate of precipitate residue become a defect. Furthermore, although preservation stability and filterability are good since the example 3 of a comparison has DBP and 24M4DBP smaller than the range, paper fixing concentration falls remarkably. Although preservation stability and paper fixing concentration are good since the example 4 of a comparison has IA, N2 SA, and CTAB smaller than the range, filterability and the rate of precipitate residue become a defect. Although the property of carbon black conforms to the range, since the ratio of a total carbon atom and all oxygen atoms is small, the example 5 of a comparison has high initial viscosity, and is remarkably poor. [of preservation stability]

[0032]

[Effect of the Invention] According to the carbon black pigment for water color ink of this invention the above passage, it can be compatible in opposite paper fixing concentration and

opposite filterability, and the water color ink in which the dispersibility continued and stabilized at the long period of time is shown further can be obtained. Therefore, it is very useful as black pigments for water color ink including the water color ink for ink jet printers.

[Translation done.]

* NOTICES *

JPO and NCIPJ are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention is excellent in underwater dispersibility ability, and relates to the carbon black pigment for water color ink suitable as an object for aqueous black ink.

[Translation done.]

* NOTICES *

JP0 and NCIP1 are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] Since wettability [as opposed to water at hydrophobicity] of carbon black is low, it is very difficult to distribute stability by high concentration to underwater. This originates in that there are very few functional groups with high compatibility with the water molecule which exists in a carbon black front face. Then, the approach of carrying out oxidation reforming of the carbon black, and forming the functional group of a hydrophilic property in a front face is learned for many years.

[0003] For example, to JP,48-18186,A, carbon black is oxidized in the water solution of the following ** halogen acid salt, and in more nearly subsequently than the system of reaction carrying out separation uptake of the oxidization carbon black, the manufacture approach of water-dispersion reforming carbon black that the manufacture approach of the oxidization carbon black characterized by washing by the organic solvent is characterized by carrying out low-temperature-oxidation plasma treatment of the carbon black to JP,57-159856,A again is indicated.

[0004] Useful [of the carbon black excellent in water-dispersion] is carried out as watercolor pigment ink, it begins a writing implement, and attracts attention also as recording ink especially for ink jet printers etc. in recent years. In the watercolor pigment ink which contains water and carbon black in JP,8-3498,A as water color ink using easy water dispersible carbon black, It sets to the manufacture approach of the watercolor pigment ink in which this carbon black has the surface activity hydrogen content of 1.5 or more mmol/g, and the watercolor pigment ink containing water and carbon black, and is (a). The process which obtains acid carbon black, and (b) The manufacture approach of the watercolor pigment ink which includes the process which oxidizes said acid carbon black further with the following ** halogen acid salt underwater is proposed. Moreover, in JP,8-319444,A, they are the oil absorption of 100ml / 100g. The manufacture approach of the watercolor pigment ink which includes process; which oxidizes this carbon black using process; and the following ** halogen acid salt which carry out differential powder of the following carbon black into an aquosity medium is indicated.

[0005] In above-mentioned JP,8-3498,A and above-mentioned JP,8-319444,A, carbon black is oxidized, and by making a front face contain many active hydrogen which is the functional group of a hydrophilic property, water-dispersion is good and obtains watercolor pigment ink excellent in prolonged distributed stability. However, in order for carbon black to distribute underwater and to maintain a stable distributed condition, it is difficult to judge the quality of dispersibility exactly only by regulating the amount of functional groups to which the amount of functional groups of the hydrophilic property which exists in the contact interface of a carbon black particle front face and a water molecule functions greatly, and only exists in per carbon black unit weight.

[0006] Then, this invention persons advanced research paying attention to the amount of hydrogen content functional groups of the hydrophilic property which considers as the new index which judges the quality of dispersibility ability exactly, and exists in per carbon black unit surface area, and developed and proposed the easy water dispersible carbon black whose amounts of total of a carboxyl group and hydroxyl are two or more 3microeq/m per unit surface area, and its manufacture approach among the hydrogen content functional groups which exist in

a front face (JP,11-148027,A).

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] According to the carbon black pigment for water color ink of this invention the above passage, it can be compatible in opposite paper fixing concentration and opposite filterability, and the water color ink in which the dispersibility continued and stabilized at the long period of time is shown further can be obtained. Therefore, it is very useful as black pigments for water color ink including the water color ink for ink jet printers.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] this invention persons advanced research about easy water dispersible carbon black succeedingly, and succeeded in development of a carbon black pigment suitable as ink for printers, such as water color ink, for example, bubble jet etc., using these easy water dispersible carbon black as a black pigment.

[0008] That is, the purpose of this invention is to offer the carbon black pigment excellent in paper fixing concentration, printing grace, regurgitation stability, lightfastness, preservation stability, etc. for water color ink, when printing to a form, an OHP sheet, art paper, etc. chiefly, a regular paper and.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] The carbon black pigment for water color ink of this invention for attaining the above-mentioned purpose 160–200m²/g and the iodine amount of adsorption (IA) 140 – 190 mg/g, [nitrogen adsorption specific surface area (N₂SA)] 0.96–1.20, and CTAB specific surface area 140–170m²/g, [the value of N₂ SA/IA] 100–140ml / 100g, and 24M4DBP oil absorption 90–110ml / 100g, [DBP oil absorption] Tinting strength (Tint) is carbon black of or more 120**, and it is characterized by the atomic ratio (reinforcement of the reinforcement / carbon to carbon bond energy of oxygen binding energy) of the total carbon atom and all the oxygen atoms which were measured by X-ray photoelectron spectroscopy being 0.1 or more on a configuration.

[0010] Moreover, the carbon black pigment for water color ink of this invention is carbon black equipped with the above-mentioned property, and the mode diameter D_{st} of stokes nominal diameter distribution of an aggregate is characterized by the value whose value of 60nm or less and mean-particle-diameter D_{upa50%} of agglomerate half-value-width ΔD_{st} in 50–70nm and an isomerism cloth is 60–110nm and maximum grain size D_{upa99%} of agglomerate having the shape of corpuscular character 250nm or less on a configuration. However, D_{st} is a centrifuge (DCF). The stokes nominal diameter of the maximum frequency in stokes nominal diameter distribution of the aggregate measured and ΔD_{st} irradiate laser light at the water dispersion of carbon black to half-value width and D_{upa50%} of this stokes nominal diameter distribution, and D_{upa99%} shows the value [in / for the value of 50% cumulative frequency in the cumulative frequency distribution curve of the agglomerate particle size created from the frequency modulation degree of the scattered light / an isomerism cloth curve] of 99% cumulative frequency.

[0011]

[Embodiment of the Invention] The property range of carbon black is regulated as mentioned above, because the paper fixing concentration at the time of printing when it considered as water color ink for N₂ SA to be under 160m²/g, and the rate of precipitate residue increased, filterability and regurgitation stability fell remarkably and 200m²/g was exceeded becomes low. Moreover, there is little volatile matter (surface functional group) of carbon black that the value of N₂ SA/IA is less than 0.96, wettability with an oxidizer water solution worsens and dispersibility falls. However, if the value of N₂ SA/IA exceeds 1.20, the unburnt matter of carbon black will cause many trouble to wettability with an oxidizer water solution, oxidation is not fully performed, but dispersibility falls.

[0012] If the area of liquid-***** becomes it small that CTAB specific surface area is under 140m²/g, and a problem is produced to filterability and the rate of precipitate residue and 170m²/g is exceeded, the area of liquid-***** will become large and dispersibility will become inadequate. DBP oil absorption is 100ml / 100g. Printing concentration becomes it thin that it is the following, and they are 140ml / 100g. If it exceeds, the rate of precipitate residue will increase and filterability will fall. 24M4DBP is 90ml / 100g. Printing concentration falls that it is the following and they are 110ml / 100g. If it exceeds, the rate of precipitate residue will increase and filterability and preservation stability will become a defect. Tint Whenever [grain / which is less than 120], since broadcloth [distribution], filterability and the rate of precipitate

residue become a defect.

[0013] In addition to these property range, the carbon black pigment of this invention is characterized by the point that the value of the atomic ratio (reinforcement of the reinforcement / carbon to carbon bond energy of oxygen binding energy) of the total carbon atom and all the oxygen atoms which were measured by X-ray photoelectron spectroscopy is 0.1 or more as an amount of functional groups which exists in the front face. When self-dispersibility [as opposed to / that the intensity ratio (atomic ratio) of the reinforcement / carbon to carbon bond energy of the oxygen binding energy measured by X-ray photoelectron spectroscopy, such as XPS and ESCA is less than 0.1 / polar solvents, such as water,] falls remarkably and considers as water color ink, preservation stability gets worse extremely. In addition, accommodation of this intensity ratio makes a carbon black particle front face oxidize chemically by oxidation treatment, and is performed by giving a hydrophilic functional group by carrying out chemical modification.

[0014] Oxidation treatment is performed by adding carbon black and oxidizing in oxidizing agent water solutions, such as alkali-metal salts, such as a hypochlorite, chlorite, a chlorate, persulfate, a perboric acid salt, and percarbonate, and ammonium salt, controls suitably the concentration of an oxidizing agent water solution, the addition of carbon black, reaction temperature, reaction time, etc., and it is processed so that the atomic ratio (reinforcement of the reinforcement / carbon to carbon bond energy of oxygen binding energy) of a total carbon atom and all oxygen atoms may become 0.1 or more.

[0015] Furthermore, the carbon black pigment for water color ink of this invention is carbon black equipped with the above-mentioned property, and it is more desirable that the value whose value of 60nm or less and mean-particle-diameter Dupa50% of agglomerate half-value-width ΔD_{50} [in / in the mode diameter D_{50} of stokes nominal diameter distribution of an aggregate / 50-70nm and an isomerism cloth] is 60-110nm and maximum grain size Dupa99% of agglomerate has the shape of corpuscular character 250nm or less.

[0016] The agglomerate particle size in a moisture powder condition becomes it small that the mode diameter D_{50} of stokes nominal diameter distribution of an aggregate is less than 50nm, whenever [black] falls, on the other hand, if 70nm is exceeded, although whenever [black] improves, the rate of precipitate residue will increase, and filterability will fall. Moreover, the diameter distribution of a grain whose half-value-width ΔD_{50} exceeds 60nm becomes broadcloth, whenever black, the rate of precipitate residue increases and filterability becomes a defect.

[0017] Moreover, as for making the value of 60-110nm and maximum grain size Dupa99% of agglomerate into the shape of corpuscular character 250nm or less, carbon black passes the value of mean-particle-diameter Dupa50% of agglomerate from the clearance between paper fiber as Dupa50% of value is less than 60nm, and paper fixing concentration falls. Although whenever [black] will improve on the other hand if 110nm is exceeded, it is for filterability and the rate of precipitate residue to get worse. Moreover, if Dupa99% of value exceeds 250nm, the rate of precipitate residue will increase and regurgitation stability and a filterable fall will become remarkable.

[0018] In addition, the value from which mean-particle-diameter Dupa50% of this agglomerate and maximum grain size Dupa99% were obtained by the following measuring method is used. Carbon black is distributed in water and it is 0.1 - 0.5 g/l. Dispersion liquid are prepared, laser light is irradiated at dispersion liquid using a heterodyne laser Doppler system particle-size-distribution measuring device (micro truck company make, UPAmode19340), and the particle size of the agglomerate in dispersion liquid is measured from the degree of the frequency modulation of the scattered light. Brownian motion of the carbon black in dispersion liquid is carried out, and the frequency of the scattered light becomes irregular with the magnitude of the carbon black floc currently distributed according to the Doppler effect. Therefore, since the violence of the Brownian motion by the magnitude of floc differs, the magnitude of the floc in the condition of distributing underwater, i.e., the particle size of agglomerate, can be measured. Thus, the cumulative frequency distribution curve is created from the measured agglomerate particle size, and mean-particle-diameter Dupa50% of agglomerate (nm) and the value of 99% cumulative

frequency are made into maximum grain size Dupa99% of agglomerate (nm) for the value of cumulative frequency 50%.

[0019] Water color ink is obtained by making it distribute by desired concentration in aqueous media, such as water, by using carbon black equipped with these properties as a black pigment. That is, pH of the water dispersion which distributed carbon black is adjusted to 6–11, and separation purification of the residual salt is carried out by electrodialysis or demarcation membranes (a reverse osmotic membrane, ultrafiltration membrane, loose R.O, etc.). In addition, the residual salt concentration in carbon black dispersion liquid makes carbon black content concentration 20%, and conductivity is 5 mS/cm. It is desirable to carry out separation purification so that it may become the following. Moreover, in order to plan distributed stability as water color ink, it is desirable to adjust a ** carbon black pigment to the concentration not more than 60wt%.

[0020] Hereafter, the example of this invention is concretely explained as contrasted with the example of a comparison.

[0021] Carbon black 100g of the property shown in one to examples 1–3 and example of comparison 4 table 1 It adds in 3000ml of persulfuric acid soda water solutions with a concentration of 2.2 Ns, and they are the reaction temperature of 60 degrees C, reaction-time 10 hours, and agitating speed 300rpm. It oxidized. Subsequently, the carbon black carried out the ** exception was distributed in pure water, the sodium-hydroxide water solution neutralized, after separating the salt which carries out purification processing by ultrafiltration membrane, and remains, it filtered and carbon black was separated, rinsing desiccation was carried out and the sample of a carbon black pigment was produced. They are oxygen binding energy reinforcement and carbon to carbon bond energy intensity about these carbon black samples Surface Science Instruments Shrine make It measured with S-Probe ESCA 2803 mold, and the atomic ratio of a total carbon atom and all oxygen atoms was written together to Table 1.

[0022] It oxidized by example of comparison 5 ozone, and also the carbon black sample was produced by the same approach as an example, the binding energy was measured, and the atomic ratio of a total carbon atom and all oxygen atoms was written together to Table 1.

[0023]

[Table 1]

| 例No. 特性 | 実 施 例 | | | 比 較 例 | | | | |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| IA | 144 | 180 | 173 | 120 | 123 | 160 | 130 | 144 |
| N ₂ SA | 170 | 178 | 181 | 135 | 119 | 160 | 134 | 170 |
| N ₂ SA/IA | 1.181 | 0.989 | 1.046 | 1.125 | 0.967 | 1.000 | 1.031 | 1.181 |
| CTAB | 160 | 152 | 159 | 128 | 111 | 150 | 130 | 160 |
| DBP | 115 | 131 | 130 | 56 | 123 | 65 | 104 | 115 |
| 24M4DBP | 100 | 98 | 101 | 49 | 92 | 58 | 90 | 100 |
| Tint | 141 | 137 | 131 | 145 | 126 | 140 | 129 | 141 |
| Dst (nm) | 61 | 58 | 69 | 47 | 68 | 50 | 62 | 61 |
| ΔDst (nm) | 44 | 40 | 51 | 32 | 40 | 35 | 48 | 44 |
| Dupa50%(nm) | 90.5 | 96.3 | 106.3 | 41.5 | 132.1 | 32.1 | 124.5 | 265.4 |
| Dupa99%(nm) | 195.4 | 214.2 | 230.1 | 162.3 | 329.2 | 145.2 | 254.1 | 457.1 |
| 原子比 | 0.34 | 0.33 | 0.35 | 0.33 | 0.32 | 0.33 | 0.34 | 0.05 |

[0024] Next, these carbon black samples were distributed by 20% of the weight of concentration in pure water as a pigment, water color ink was prepared, and the following approach estimated dispersibility ability and the ink engine performance. The obtained result was shown in Table 2.

[0025] ** warming — stability; — a sample — a well-closed container — putting — the inside of a 70-degree C attemperator — the viscosity change for one to four weeks — measuring — warming — the distributed stability at the time was compared. In addition, viscosity was measured with the rotational-vibration type viscometer [Yamaichi Electronics make and VM-100 A-L].

[0026] ** particle diameter measurement; — a sample and warming — it measured using the heterodyne laser Doppler system particle-size-distribution measuring device [micro truck company make and UPA model9340] about the particle diameter of the sample which examined stability. If a laser beam is applied to the particle which is carrying out Brownian motion into suspension, the frequency of the scattered light will modulate this measuring device according to the Doppler effect. The violence of Brownian motion, i.e., particle diameter, is measured from the modulation degree of the frequency.

[0027] ** Printing concentration; the carbon black distribution concentration of water color ink is diluted to 4% of the weight, use XEROX 4024 paper as copy paper, print by #6 bar coder to this, and it is Macbeth concentration meter [COL mho gene company make. Optical density was measured using RD-927].

[0028] ** Filterability; watercolor pigment ink 200g The filter paper (NO.2) and film aperture of 90phi 3 micrometers 0.8 mum and 0.65 micrometers 0.45 micrometers The filtration trial was performed under reduced pressure of 20Torr(s) using the filter, and through put was measured.

[0029] ** rate of precipitate residue; — weight ratio (M1/M0) of the amount of precipitate residue (M1) after performing at-long-intervals alignment separation processing for aquosity black ink with the gravitational acceleration of 20000G for 30 minutes, and the weight (M0) of the carbon black before centrifugal separation processing It considered as the rate of precipitate residue. Distributed stability becomes good, so that this value is low.

[0030]

[Table 2]

| 例No. | | 実 施 例 | | | 比 較 例 | | | | |
|-----------------------|---------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| 保 存 安 定 性 | 初期粘度(cp) | 3.34 | 3.65 | 3.12 | 2.54 | 3.14 | 3.34 | 3.65 | 8.51 |
| | 70℃、1 W後(cp) | 3.34 | 3.65 | 3.11 | 2.54 | 3.14 | 3.34 | 3.65 | ゲル化 |
| | 70℃、2 W後(cp) | 3.31 | 3.65 | 3.10 | 2.53 | 3.13 | 3.31 | 3.65 | — |
| | 70℃、3 W後(cp) | 3.30 | 3.59 | 3.08 | 2.53 | 3.13 | 3.30 | 3.59 | — |
| | 70℃、4 W後(cp) | 3.28 | 3.57 | 3.07 | 2.53 | 3.13 | 3.28 | 3.57 | — |
| 平 均 粒 径 | 初期平均粒径(nm) | 90.5 | 96.3 | 106.3 | 41.5 | 132.1 | 32.1 | 124.5 | 265.4 |
| | 70℃、1 W後(nm) | 90.1 | 96.2 | 106.2 | 41.5 | 131.8 | 32.1 | 124.5 | ゲル化 |
| | 70℃、2 W後(nm) | 89.9 | 96.1 | 106.2 | 41.4 | 131.7 | 32.1 | 124.4 | — |
| | 70℃、3 W後(nm) | 89.7 | 96.1 | 106.2 | 41.3 | 131.7 | 32.0 | 124.3 | — |
| | 70℃、4 W後(nm) | 89.5 | 96.1 | 106.1 | 41.2 | 131.5 | 32.0 | 124.3 | — |
| 最 大 粒 径 | 初期最大粒径(nm) | 195.4 | 214.2 | 230.1 | 162.3 | 329.2 | 145.2 | 254.1 | 457.1 |
| | 70℃、1 W後(nm) | 195.3 | 214.2 | 230.0 | 162.1 | 329.1 | 145.2 | 254.1 | ゲル化 |
| | 70℃、2 W後(nm) | 195.3 | 214.1 | 229.9 | 161.9 | 328.8 | 145.2 | 254.1 | — |
| | 70℃、3 W後(nm) | 195.2 | 214.1 | 229.8 | 161.8 | 328.8 | 145.1 | 254.0 | — |
| | 70℃、4 W後(nm) | 195.2 | 214.0 | 229.8 | 161.7 | 328.8 | 145.1 | 254.0 | — |
| 濾 過 性 % | No.2濾紙 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 0 |
| | 膜孔径 (3 μm) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 0 |
| | 膜孔径 (0.8 μm) | 100 | 100 | 100 | 100 | 80 | 100 | 100 | 0 |
| | 膜孔径 (0.65 μm) | 100 | 100 | 100 | 100 | 0 | 100 | 5 | 0 |
| | 膜孔径 (0.45 μm) | 50 | 80 | 45 | 50 | 0 | 70 | 0 | 0 |
| 印字濃度； コピー紙 (OD値) | | 1.41 | 1.45 | 1.46 | 0.98 | 1.47 | 0.92 | 1.44 | 1.58 |
| 沈殿残渣率 (%) | | 11.3 | 14.5 | 17.9 | 12.5 | 27.1 | 11.1 | 24.1 | 67.2 |

[0031] although the water color ink which was distributed and prepared the carbon black pigment of an example from the result of Tables 1 and 2 has the outstanding preservation stability, filterability, paper fixing concentration, and a rate of precipitate residue — the example 1 of a comparison — IA, N2 SA, CTAB, DBP, and 24M4 — although filterability, preservation stability, and the rate of precipitate residue are good since DBP and Dst are also small, paper fixing concentration is remarkably low. Although preservation stability and paper fixing concentration are good since the example 2 of a comparison has IA, N2 SA, and CTAB out of range, filterability and the rate of precipitate residue become a defect. Furthermore, although preservation stability and filterability are good since the example 3 of a comparison has DBP and 24M4DBP smaller than the range, paper fixing concentration falls remarkably. Although preservation stability and paper fixing concentration are good since the example 4 of a comparison has IA, N2 SA, and CTAB smaller than the range, filterability and the rate of precipitate residue become a defect. Although the property of carbon black conforms to the range, since the ratio of a total carbon atom and all oxygen atoms is small, the example 5 of a comparison has high initial viscosity, and is remarkably poor. [of preservation stability]

[0032]

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2001-81355

(P2001-81355A)

(43) 公開日 平成13年3月27日 (2001.3.27)

| (51) Int.Cl. ⁷ | 識別記号 | F I | テーマコード (参考) |
|---------------------------|------|---------------|-------------|
| C 0 9 C 1/56 | | C 0 9 C 1/56 | 4 J 0 3 7 |
| C 0 9 D 11/02 | | C 0 9 D 11/02 | 4 J 0 3 9 |

審査請求 未請求 請求項の数2 OL (全 6 頁)

(21) 出願番号 特願平11-263497
 (22) 出願日 平成11年9月17日 (1999.9.17)

(71) 出願人 000219576
 東海カーボン株式会社
 東京都港区北青山1丁目2番3号
 (72) 発明者 新井 啓哲
 東京都港区北青山1丁目2番3号 東海カーボン株式会社内
 (72) 発明者 河野 正孝
 東京都港区北青山1丁目2番3号 東海カーボン株式会社内
 (74) 代理人 100071663
 弁理士 福田 保夫 (外1名)

最終頁に続く

(54) 【発明の名称】 水性インキ用カーボンブラック顔料

(57) 【要約】

【課題】 水中への分散性能に優れ、水性黒色インキ用として好適なカーボンブラック顔料を提供する。

【解決手段】 本発明の水性インキ用カーボンブラック顔料は N_2SA 160~200 m^2/g 、 IA 140~190 mg/g 、 N_2SA/IA 0.96 ~1.20、 $CTAB$ 140~170 m^2/g 、 DBP 100~140 $ml/100g$ 、 $24M4DBP$ 90~110 $ml/100g$ 、 $Tint$ 120以上、のカーボンブラックであって、X線光電子分光法により測定した全炭素原子と全酸素原子との原子比 (酸素結合エネルギーの強度/炭素結合エネルギーの強度) が 0.1以上であることを特徴とする。更に、アグリゲートのストークス相当径分布のモード径 D_{st} が 50~70 nm 、半値幅 ΔD_{st} が 60 nm 以下、アグロメレート of 平均粒径 $D_{upa50\%}$ の値が 60~110 nm 、アグロメレートの最大粒径 $D_{upa99\%}$ の値が 250 nm 以下の粒子性状を有するものである。

(2)

【特許請求の範囲】

【請求項1】 窒素吸着比表面積(N_2SA)が $160 \sim 200 \text{ m}^2/\text{g}$ 、沃素吸着量(IA)が $140 \sim 190 \text{ mg/g}$ 、 N_2SA/IA の値が $0.96 \sim 1.20$ 、CTAB比表面積が $140 \sim 170 \text{ m}^2/\text{g}$ 、DBP吸油量が $100 \sim 140 \text{ ml/100g}$ 、24M4DBP吸油量が $90 \sim 110 \text{ ml/100g}$ 、着色力(Tint)が120以上、のカーボンブラックであって、X線光電子分光法により測定した全炭素原子と全酸素原子との原子比(酸素結合エネルギーの強度/炭素結合エネルギーの強度)が0.1以上であることを特徴とする水性インキ用カーボンブラック顔料。

【請求項2】 アグリゲートのストークス相当径分布のモード径D_{st}が $50 \sim 70 \text{ nm}$ 、同分布における半値幅 ΔD_{st} が 60 nm 以下、アグロメレート平均粒径D_{upa50%}の値が $60 \sim 110 \text{ nm}$ 、アグロメレートの最大粒径D_{upa99%}の値が 250 nm 以下の粒子性状を有する、請求項1記載の水性インキ用カーボンブラック顔料。但し、D_{st}は遠心沈降法(DCF)により測定されるアグリゲートのストークス相当径分布における最大頻度のストークス相当径、 ΔD_{st} は同ストークス相当径分布の半値幅、また、D_{upa50%}はカーボンブラックの水分散液にレーザー光を照射し、散乱光の周波数変調度合から作成したアグロメレート粒径の累積度数分布曲線における50%累積度数の値を、D_{upa99%}は同分布曲線における99%累積度数の値を示す。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、水中への分散性能に優れ、水性黒色インキ用として好適な水性インキ用カーボンブラック顔料に関する。

【0002】

【従来の技術】カーボンブラックは疎水性で水に対する濡れ性が低いため水中に高濃度で安定に分散させることが極めて困難である。これはカーボンブラック表面に存在する水分子との親和性が高い官能基が極めて少ないことに起因する。そこで、カーボンブラックを酸化改質して表面に親水性の官能基を形成する方法が古くから知られている。

【0003】例えば、特開昭48-18186号公報にはカーボンブラックを次亜ハロゲン酸塩の水溶液で酸化処理し、ついで反応系より酸化カーボンブラックを分離捕集するにあたり有機溶剤で洗浄することの特徴とする酸化カーボンブラックの製造方法が、また、特開昭57-159856号公報にはカーボンブラックを低温酸化プラズマ処理することの特徴とする水分散性改質カーボンブラックの製造方法が開示されている。

【0004】水分散性に優れたカーボンブラックは水性顔料インキとして有用されており、筆記具をはじめ、特に近年ではインキジェットプリンター用の記録液などとしても注目されている。易水分散性カーボンブラックを

2

用いた水性インキとして、例えば、特開平8-3498号公報には水とカーボンブラックとを含有する水性顔料インキにおいて、該カーボンブラックが 1.5 mmol/g 以上の表面活性水素含有量を有する水性顔料インキ、及び、水とカーボンブラックとを含有する水性顔料インキの製造方法において、(a) 酸性カーボンブラックを得る工程と、(b) 前記酸性カーボンブラックを水中で次亜ハロゲン酸塩で更に酸化する工程とを、包含する水性顔料インキの製造方法が提案されている。また、特開平8-319444号公報には吸油量 100 ml/100g 以下のカーボンブラックを水性媒体中に微分散する工程；及び次亜ハロゲン酸塩を用いて該カーボンブラックを酸化する工程；を包含する水性顔料インキの製造方法が開示されている。

【0005】上記の特開平8-3498号公報及び特開平8-319444号公報ではカーボンブラックを酸化して、表面に親水性の官能基である活性水素を多く含有させることにより水分散性が良好で、長期間の分散安定性に優れた水性顔料インキを得るものである。しかしながら、カーボンブラックが水中に分散して安定な分散状態を維持するためにはカーボンブラック粒子表面と水分子との接触界面に存在する親水性の官能基量が大きく機能し、単にカーボンブラック単位重量当たり存在する官能基量を規制するのみでは分散性の良否を的確に判断することは困難である。

【0006】そこで、本発明者らは分散性能の良否を的確に判断する新たな指標としてカーボンブラック単位表面積当たり存在する親水性の水素含有官能基量に着目して研究を進め、表面に存在する水素含有官能基のうちカルボキシル基とヒドロキシル基の総和量が、単位表面積当たり $3 \mu \text{ eq/m}^2$ 以上である易水分散性カーボンブラック、及びその製造方法を開発、提案した(特開平11-148027号公報)。

【0007】

【発明が解決しようとする課題】本発明者らは、引き続き易水分散性カーボンブラックについて研究を進め、これらの易水分散性カーボンブラックを黒色顔料として用いた水性インキ、例えばバブルジェットなどのプリンター用インキとして好適なカーボンブラック顔料の開発に成功した。

【0008】すなわち、本発明の目的は、普通紙、専用紙、OHPシート、アート紙などに印字する場合に、紙定着濃度、印字品位、吐出安定性、耐光性、保存安定性などに優れた水性インキ用のカーボンブラック顔料を提供することにある。

【0009】

【課題を解決するための手段】上記目的を達成するための本発明の水性インキ用カーボンブラック顔料は、窒素吸着比表面積(N_2SA)が $160 \sim 200 \text{ m}^2/\text{g}$ 、沃素吸着量(IA)が $140 \sim 190 \text{ mg/g}$ 、 N_2SA/IA の値が0.1

(3)

3

96~1.20、CTAB比表面積が140~170m²/g、DBP吸油量が100~140ml/100g、24M4DBP吸油量が90~110ml/100g、着色力(Tint)が120以上、のカーボンブラックであって、X線光電子分光法により測定した全炭素原子と全酸素原子との原子比(酸素結合エネルギーの強度/炭素結合エネルギーの強度)が0.1以上であることを構成上の特徴とする。

【0010】また、本発明の水性インキ用カーボンブラック顔料は、上記の特性を備えたカーボンブラックであって、アグリゲートのストークス相当径分布のモード径D_{st}が50~70nm、同分布における半値幅ΔD_{st}が60nm以下、アグロメレートの平均粒径Dupa50%の値が60~110nm、アグロメレートの最大粒径Dupa99%の値が250nm以下の粒子性状を有することを構成上の特徴とする。但し、D_{st}は遠心沈降法(DCF)により測定されるアグリゲートのストークス相当径分布における最大頻度のストークス相当径、ΔD_{st}は同ストークス相当径分布の半値幅、また、Dupa50%はカーボンブラックの水分散液にレーザー光を照射し、散乱光の周波数変調度合いから作成したアグロメレート粒径の累積度数分布曲線における50%累積度数の値を、Dupa99%は同分布曲線における99%累積度数の値を示す。

【0011】

【発明の実施の形態】上記のようにカーボンブラックの特性範囲を規制するのは、N₂SAが160m²/g未満であると水性インキとした場合に沈殿残渣率が增大して、濾過性、吐出安定性が著しく低下し、200m²/gを越えると印字した際の紙定着濃度が低くなるためである。また、N₂SA/IAの値が0.96未満であるとカーボンブラックの揮発分(表面官能基)が少なく、酸化剤水溶液との濡れ性が悪くなって分散性が低下する。しかしN₂SA/IAの値が1.20を越えるとカーボンブラックの未燃分が多く酸化剤水溶液との濡れ性に支障を来し、酸化が充分に行われず分散性が低下する。

【0012】CTAB比表面積が140m²/g未満であると液-固界面の面積が小さくなり、濾過性、沈殿残渣率に問題を生じ、また170m²/gを越えると液-固界面の面積が大きくなり分散性が不十分になる。DBP吸油量が100ml/100g未満であると印字濃度が薄くなり、140ml/100gを越えると沈殿残渣率が増加し、濾過性が低下する。24M4DBPが90ml/100g未満であると印字濃度が低下し、110ml/100gを越えると沈殿残渣率が増加して、濾過性、保存安定性が不良になる。Tintが120未満であると粒度分布がブロードなため、濾過性、沈殿残渣率が不良になる。

【0013】本発明のカーボンブラック顔料は、これらの特性範囲に加えて、その表面に存在する官能基量として、X線光電子分光法により測定した全炭素原子と全酸素原子との原子比(酸素結合エネルギーの強度/炭素結合エネルギーの強度)の値が0.1以上である点を特徴

4

としている。XPSやESCAなどのX線光電子分光法により測定される酸素結合エネルギーの強度/炭素結合エネルギーの強度比(原子比)が、0.1未満であると、水などの極性溶媒に対する自己分散性が著しく低下し、水性インキとした場合に保存安定性が極めて悪化する。なお、この強度比の調節は酸化処理によりカーボンブラック粒子表面を化学的に酸化反応させ、化学修飾することにより親水性官能基を付与することにより行われる。

【0014】酸化処理は、例えば次亜塩素酸塩、亜塩素酸塩、塩素酸塩、過硫酸塩、過硼酸塩、過炭酸塩などのアルカリ金属塩やアンモニウム塩などの酸化剤水溶液中にカーボンブラックを添加して酸化することにより行われ、酸化剤水溶液の濃度、カーボンブラックの添加量、反応温度、反応時間などを適宜に制御して、全炭素原子と全酸素原子との原子比(酸素結合エネルギーの強度/炭素結合エネルギーの強度)が0.1以上となるように処理される。

【0015】更に、本発明の水性インキ用カーボンブラック顔料は、上記の特性を備えたカーボンブラックであって、アグリゲートのストークス相当径分布のモード径D_{st}が50~70nm、同分布における半値幅ΔD_{st}が60nm以下、アグロメレートの平均粒径Dupa50%の値が60~110nm、アグロメレートの最大粒径Dupa99%の値が250nm以下の粒子性状を有することがより好ましい。

【0016】アグリゲートのストークス相当径分布のモード径D_{st}が50nm未満であると水分散状態でのアグロメレート粒径が小さくなって、黒色度が低下し、一方、70nmを越えると黒色度は向上するが沈殿残渣率が増加して、濾過性が低下する。また、半値幅ΔD_{st}が60nmを越えると粒径分布がブロードになり、黒色度、沈殿残渣率が増加し、濾過性が不良になる。

【0017】また、アグロメレートの平均粒径Dupa50%の値を60~110nm、アグロメレートの最大粒径Dupa99%の値を250nm以下の粒子性状とするのは、Dupa50%の値が60nm未満であると紙繊維の隙間からカーボンブラックが通過し、紙定着濃度が低下する。一方110nmを越えると黒色度は向上するが、濾過性および沈殿残渣率が悪化するためである。また、Dupa99%の値が250nmを越えると沈殿残渣率が增大して、吐出安定性および濾過性の低下が著しくなる。

【0018】なお、このアグロメレートの平均粒径Dupa50%、最大粒径Dupa99%は、下記の測定方法によって得られた値が用いられる。カーボンブラックを水に分散して0.1~0.5g/lの分散液を調製し、ヘテロダインレーザドブレンダー方式粒度分布測定装置(マイクロトラック社製、UPAmode19340)を用いて分散液にレーザー光を照射して、散乱光の周波数変調の度合いから分散液中のアグロメレートの粒径を測定する。分散液中のカーボ

(4)

5

ンブラックはブラウン運動しており、ドップラー効果によって分散しているカーボンブラック凝集体の大きさにより散乱光の周波数が変調する。したがって、凝集体の大きさによるブラウン運動の激しさが異なることから、水中に分散している状態における凝集体の大きさ、すなわちアグロメレート粒径を測定することができる。このようにして測定したアグロメレート粒径からその累積度数分布曲線を作成し、50%累積度数の値をアグロメレートの平均粒径Dupa50%(nm)、99%累積度数の値をアグロメレートの最大粒径Dupa99%(nm)とする。

【0019】これらの特性を備えたカーボンブラックを黒色顔料として、水などの水性媒体中に所望の濃度で分散させることにより水性インキが得られる。すなわち、カーボンブラックを分散させた水分散液のpHを6～11に調節し、電気透析あるいは分離膜（逆浸透膜、限外濾過膜、ルーズ R.0など）で残塩を分離精製する。なお、カーボンブラック分散液中の残塩濃度はカーボンブラック含有濃度を20%として導電度が5mS/cm未満となるように分離精製することが好ましい。また、水性インキとして分散安定性を図るために、はカーボンブラック顔料を60wt%以下の濃度に調整することが望ましい。

6

*【0020】以下、本発明の実施例を比較例と対比して具体的に説明する。

【0021】実施例1～3、比較例1～4

表1に示す特性のカーボンブラック100gを濃度2、2Nの過硫酸ソーダ水溶液3000mlに添加し、反応温度60℃、反応時間10時間、攪拌速度300rpmで酸化処理した。次いで、濾別したカーボンブラックを純水中に分散させて水酸化ナトリウム水溶液で中和し、限外濾過膜により精製処理して残存する塩を分離したのち、濾過してカーボンブラックを分離し、水洗乾燥してカーボンブラック顔料の試料を作製した。これらのカーボンブラック試料について酸素結合エネルギー強度と炭素結合エネルギー強度をSurface Science Instruments社製S-Prove ESCA 2803型により測定し、全炭素原子と全酸素原子との原子比を表1に併記した。

【0022】比較例5

オゾンにより酸化処理したほかは、実施例と同じ方法によりカーボンブラック試料を作製し、その結合エネルギーを測定して、全炭素原子と全酸素原子との原子比を表1に併記した。

【0023】

【表1】

| 例No. 特性 | 実 施 例 | | | 比 較 例 | | | | |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| IA | 144 | 180 | 173 | 120 | 123 | 160 | 130 | 144 |
| N ₂ SA | 170 | 178 | 181 | 135 | 119 | 160 | 134 | 170 |
| N ₂ SA/IA | 1.181 | 0.989 | 1.046 | 1.125 | 0.967 | 1.000 | 1.031 | 1.181 |
| CTAB | 160 | 152 | 159 | 128 | 111 | 150 | 130 | 160 |
| DBP | 115 | 131 | 130 | 56 | 123 | 65 | 104 | 115 |
| 24M4DBP | 100 | 98 | 101 | 49 | 92 | 58 | 90 | 100 |
| Tint | 141 | 137 | 131 | 145 | 126 | 140 | 129 | 141 |
| Dst (nm) | 61 | 58 | 69 | 47 | 68 | 50 | 62 | 61 |
| Δ Dst (nm) | 44 | 40 | 51 | 32 | 40 | 35 | 48 | 44 |
| Dupa50%(nm) | 90.5 | 96.3 | 106.3 | 41.5 | 132.1 | 32.1 | 124.5 | 265.4 |
| Dupa99%(nm) | 195.4 | 214.2 | 230.1 | 162.3 | 329.2 | 145.2 | 254.1 | 457.1 |
| 原子比 | 0.34 | 0.33 | 0.35 | 0.33 | 0.32 | 0.33 | 0.34 | 0.05 |

【0024】次に、これらのカーボンブラック試料を顔料として純水中に20重量%の濃度で分散させて水性インキを調製し、下記の方法により分散性能及びインキ性能を評価した。得られた結果を表2に示した。

【0025】①加温安定性；サンプルを密閉容器に詰め、70℃の保温器中にて1週間から4週間の粘度変化を測定して、加温時の分散安定性を比較した。なお、粘度は回転振動式粘度計〔山一電機（株）製、VM-100A-L

(5)

7

)により測定した。

【0026】②粒子径測定；サンプル及び加温安定性の試験を行ったサンプルの粒子径についてヘテロダインレーザドップラー方式粒度分布測定装置〔マイクロトラック社製、UPA model9340〕を用いて測定した。この測定装置は、懸濁液中においてブラウン運動している粒子にレーザ光を当てると、ドップラー効果により散乱光の周波数に変調する。その周波数の変調度合いからブラウン運動の激しさ、すなわち粒子径を測定するものである。

【0027】③印字濃度；水性インキのカーボンブラック分散濃度を4重量%に希釈し、コピー紙としてXEROX 4024紙を使用し、これに#6バーコードにより印字して、マクベス濃度計〔コルモーゲン社製 RD-927〕を用いて*

8

* 光学濃度を測定した。

【0028】④濾過性；水性顔料インキ200gを90φの濾紙 (NO.2) 及び膜孔径 3μm、0.8μm、0.65μm、0.45μmのフィルターを用いて20Torrの減圧下で濾過試験を行い通過量を測定した。

【0029】⑤沈殿残渣率；水性黒色インキを20000Gの重力加速度で30分間遠心分離処理を行った後の沈殿残渣量(M₁)と、遠心分離処理前のカーボンブラックの重量(M₀)との重量比(M₁/M₀)を沈殿残渣率とした。この値が低いほど分散安定性は良好になる。

【0030】

【表2】

| 例No. | | 実施例 | | | 比較例 | | | | |
|---------------------|---------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| 保存安定性 | 初期粘度(cp) | 3.34 | 3.65 | 3.12 | 2.54 | 3.14 | 3.34 | 3.65 | 8.51 |
| | 70℃、1W後(cp) | 3.34 | 3.65 | 3.11 | 2.54 | 3.14 | 3.34 | 3.65 | ゲル化 |
| | 70℃、2W後(cp) | 3.31 | 3.65 | 3.10 | 2.53 | 3.13 | 3.31 | 3.65 | — |
| | 70℃、3W後(cp) | 3.30 | 3.59 | 3.08 | 2.53 | 3.13 | 3.30 | 3.59 | — |
| | 70℃、4W後(cp) | 3.28 | 3.57 | 3.07 | 2.53 | 3.13 | 3.28 | 3.57 | — |
| 平均粒径 | 初期平均粒径(nm) | 90.5 | 96.3 | 106.3 | 41.5 | 132.1 | 32.1 | 124.5 | 265.4 |
| | 70℃、1W後(nm) | 90.1 | 96.2 | 106.2 | 41.5 | 131.8 | 32.1 | 124.5 | ゲル化 |
| | 70℃、2W後(nm) | 89.9 | 96.1 | 106.2 | 41.4 | 131.7 | 32.1 | 124.4 | — |
| | 70℃、3W後(nm) | 89.7 | 96.1 | 106.2 | 41.3 | 131.7 | 32.0 | 124.3 | — |
| | 70℃、4W後(nm) | 89.5 | 96.1 | 106.1 | 41.2 | 131.5 | 32.0 | 124.3 | — |
| 最大粒径 | 初期最大粒径(nm) | 195.4 | 214.2 | 230.1 | 162.3 | 328.2 | 145.2 | 254.1 | 457.1 |
| | 70℃、1W後(nm) | 195.3 | 214.2 | 230.0 | 162.1 | 329.1 | 145.2 | 254.1 | ゲル化 |
| | 70℃、2W後(nm) | 195.3 | 214.1 | 229.9 | 161.9 | 328.8 | 145.2 | 254.1 | — |
| | 70℃、3W後(nm) | 195.2 | 214.1 | 229.8 | 161.8 | 328.8 | 145.1 | 254.0 | — |
| | 70℃、4W後(nm) | 195.2 | 214.0 | 229.8 | 161.7 | 328.8 | 145.1 | 254.0 | — |
| 濾過性 % | No.2濾紙 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 0 |
| | 膜孔径 (3 μm) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 0 |
| | 膜孔径 (0.8 μm) | 100 | 100 | 100 | 100 | 80 | 100 | 100 | 0 |
| | 膜孔径 (0.65 μm) | 100 | 100 | 100 | 100 | 0 | 100 | 5 | 0 |
| | 膜孔径 (0.45 μm) | 50 | 60 | 45 | 50 | 0 | 70 | 0 | 0 |
| 印字濃度； コピー紙 (OD値) | | 1.41 | 1.45 | 1.46 | 0.98 | 1.47 | 0.92 | 1.44 | 1.58 |
| 沈殿残渣率 (%) | | 11.3 | 14.5 | 17.9 | 12.5 | 27.1 | 11.1 | 24.1 | 67.2 |

【0031】表1、2の結果から、実施例のカーボンブラック顔料を分散させて調製した水性インキは、優れた保存安定性、濾過性、紙定着濃度、沈殿残渣率を兼ね備えているが、比較例1はIA、N₂ SA、CTAB、DBP、24M4DBP、Dstも小さいため濾過性、保存安定性、沈殿残渣率は良好であるが、紙定着濃度が著しく

低い。比較例2はIA、N₂ SA、CTABが範囲外であるため保存安定性、紙定着濃度は良好であるが、濾過性、沈殿残渣率が不良になる。更に、比較例3はDBP、24M4DBPが範囲より小さいため保存安定性、濾過性は良好であるが、紙定着濃度が著しく低下する。比較例4はIA、N₂ SA、CTABが範囲より小さい

(6)

9

め保存安定性、紙定着濃度は良好であるが、濾過性、沈殿残渣率が不良になる。比較例5はカーボンブラックの特性は範囲に適合しているが、全炭素原子と全酸素原子との比が小さいため初期粘度が高く、保存安定性が著しく不良である。

【0032】

10

【発明の効果】以上のとおり、本発明の水性インキ用カーボンブラック顔料によれば、相反する紙定着濃度と濾過性を両立し、更に、長期に亘り安定した分散性を示す水性インキを得ることができる。したがって、インキジェットプリンター用の水性インキをはじめとする水性インキ用の黒色顔料として極めて有用である。

フロントページの続き

Fターム(参考) 4J037 AA02 CA15 DD05 DD07 DD17
DD20 EE02 EE19 EE28 EE43
FF05 FF15 FF30
4J039 BA04 BE01 CA06 EA19 EA35
EA42 EA43 EA44 FA02 GA24